TITLE: Field Dependence of the Spin Reorientation Temperature in Micro- and Nanocrystalline Forms of $Nd_2Fe_{14}B$

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ABSTRACT: Insight into the anisotropy behavior of $Nd_2Fe_{14}B$ may be obtained by measurements of the spin reorientation temperature T_S where the overall magnetocrystalline anisotropy changes to allow the magnetic moment to relax from an easy axis to an easy cone configuration. DC magnetization measurements made at various applied fields on sintered and nanocrystalline forms of $Nd_2Fe_{14}B$ indicate a T_S that remains constant for the sintered sample but is strongly field-dependent for the nanocrystalline forms of the material. Specifically, T_S decreases with decreasing applied fields of strengths 5 T, 1 T and 0.01 T. A simple model that minimizes the total energy of the system leads to the conclusion that the spin reorientation temperature is insensitive to applied field. Therefore it is concluded that the apparent decrease in the system's spin reorientation temperatures with decrease in measuring field can be attributed to the nanoscale structure of the system and a difference in the anisotropy constants compared to their bulk values.

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FIELD DEPENDENCE OF THE SPIN REORIENTATION TEMPERATURE IN MICRO- AND NANOCRYSTALLINE FORMS OF $Nd_2Fe_{14}B$

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Insight into the anisotropy behaviour of $Nd_2Fe_{14}B$ may be obtained by measurements of the spin reorientation temperature T_S where the overall magnetocrystalline anisotropy changes to allow the magnetic moment to relax from an easy-axis to an easy-cone configuration. DC magnetisation measurements made at various applied fields on single crystal, sintered and nanocrystalline forms of $Nd_2Fe_{14}B$ indicate a T_S that remains constant for the sintered and single crystal samples but is strongly field-dependent for the nanocrystalline forms of the material. Specifically, T_S decreases with decreasing applied fields of strengths 5 T, 1 T and 0.1 T. A simple model that minimizes the total energy of the system leads to the conclusion that the spin reorientation temperature is insensitive to applied field. Therefore it is concluded that the apparent decrease in the system's spin reorientation temperatures with decrease in measuring field can be attributed to the nanoscale structure of the system and a difference in the anisotropy constants compared to their bulk values.

1 Introduction

The $Nd_2Fe_{14}B$ spin reorientation temperature T_s is the temperature at which the easy magnetization direction changes from axial alignment to cone alignment about the tetragonal c-axis. It occurs at the temperature where the sum of involved energies (the crystalline electric field, the exchange energy and the magnetostatic energy) is the same for different directions in the crystal. These energies are all thought to be intrinsic to the system, and therefore it would not be expected that the spin reorientation temperature would be sensitive to applied fields that are less than the internal fields of the system.

The T_s of $Nd_2Fe_{14}B$ (NdFeB) has been found experimentally to be within a few degrees of 135 K for single crystals [1 -3], polycrystalline [4,5] and sintered NdFeB [4,5]. This observation holds for both dc and ac magnetic measurement methods [6]. These materials are generally large grained (or single crystal) with the average grain size in the order of a few microns. However, it has been shown [4,5] that T_s of $Nd_2Fe_{14}B$ decreases with decreasing grain size. Nanocrystalline melt-spun $Nd_2Fe_{14}B$ with an average grain size of 19 nm exhibited a T_s of 117 K [4]. Kou *et al.* [4] attributed the observed decrease in the spin reorientation temperature of nanocrystalline NdFeB to strong inter-grain exchange coupling.

Iida *et al.* [7] reported a field-induced spin reorientation in $Nd_2Fe_{14}B$ single-phase oriented polycrystalline sample. They observed an increase in T_s from 143 K to 152 K on increasing the applied field from 0.1 T to 0.7 T. This current paper reports the observed dependence of the spin reorientation temperature in a range of nanoscale melt spun NdFeB materials as compared to larger-grained NdFeB and clarifies factors affecting the spin reorientation in nanoscale magnetic materials.

2 Experimental Procedures

$Nd_{13.8}Fe_{80.7}B_{5.5}$ samples were made with commercial grade materials (MQPA) provided by Magnequench International Inc. and melt spun to an overquenched state. The samples were annealed in argon at 650 °C for 4 minutes to develop a suitable microstructure with optimum coercivity. Sintered magnets were fabricated by vacuum sintering at 1080 °C for 1 hour and then post-sintered for 4 hours at temperatures ranging from 600 °C to 950 °C. The hot pressed magnet alloys were obtained from the General Motors Research and Development Center. Melt-spun ribbons were consolidated at 750 °C to form the hot-pressed sample.

Magnetization curves were measured using a SQUID magnetometer on perpendicularly aligned samples cooled in a 5 T field from 325 K down to 10 K. The applied measurement fields were 5 T, 1 T and 0.1 T. The spin reorientation temperature T_s was determined as the inflection point in the magnetization versus temperature curves, evaluated from the minimum of the derivative dM/dT [8]. An example of a typical magnetization curve and the accompanying derivative curve is given in Figure 1 for a single crystal NdFeB sample at an applied field of 1 T. Average grain sizes were determined using Cu Kα x-ray diffraction and applying the Scherrer formula (MQPA sample) or by TEM (hot pressed sample HP1553).

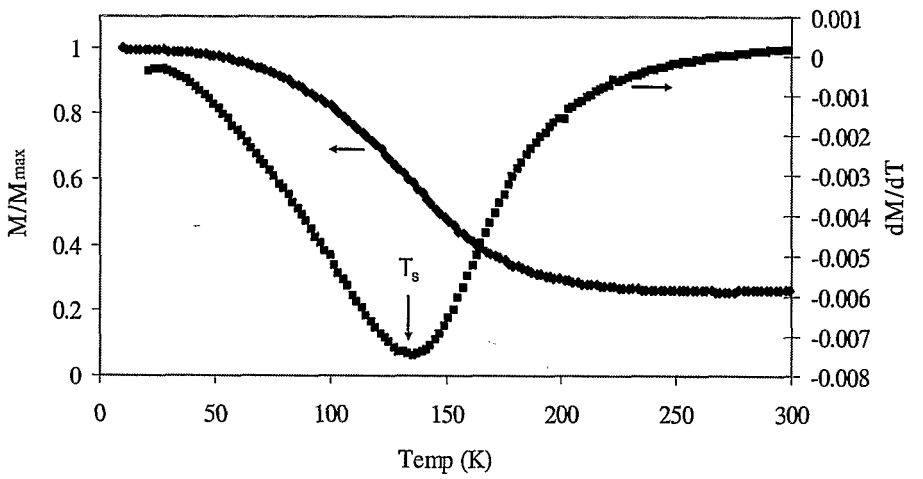

Figure 1: Typical magnetisation versus temperature curve and its derivative with respect to temperature at an applied field of 1T for the NdFeB single crystal.

3 Results and Discussion

Table 1 gives the nominal compositions, sample processing, average grain size and spin reorientation temperatures at various applied fields for the samples. Figure 2 shows the derivative of the magnetization curves for the hot-pressed NdFeB sample with various applied fields and Figure 3 shows the results for a NdFeB single crystal. Similar results were obtained for nanocrystalline NdFeB powder (MQPA) and a sintered NdFeB sample. In all cases, the dM/dT curve for an applied field of 5 T does not have a sharp minimum, probably because the small

moment change along the measuring axis at the spin reorientation temperature is masked by the large moment of the sample at large applied fields. This makes the determination of T_s more difficult for high applied fields. The apparent decrease of T_s for the sintered sample with H_{app} = 5 T is thought to be due to the broadening of the transition for this sample. The occurrence of 2 minima in the dM/dT curve of the hot-pressed sample (Fig 2 and Table 1) at H_{app} = 0.1 T is probably due to the presence of a large range of grain sizes in this sample. The values of T_s obtained in this study (see Table 1) agree well with T_s in the literature [1-3].

Table 1: Nominal compositions and spin reorientation temperatures for various applied fields.

Composition	Sample Designation	Average grain size (nm)	H_{app} (T)	T_s (K)
$Nd_{13.8}Fe_{80.7}B_{5.5}$	MQPA	34	0.01	58
			1	111
			5	117
$Nd_{15}Fe_{78.5}B_{6.5}$.	Sintered (measured perpendicular to alignment axis)	>1000	0.1	132
			1	132
			5	116
$Nd_{13.75}Fe_{80.25}B_6$	Hot-pressed HP1553 (measured parallel to alignment axis)	~100	0.01	55
			0.1	60, 137
			1	127
			5	127
$Nd_2Fe_{14}B$	Single crystal (measured perpendicular to easy direction)	-	0.01	130
			0.1	132
			1	135
			5	133

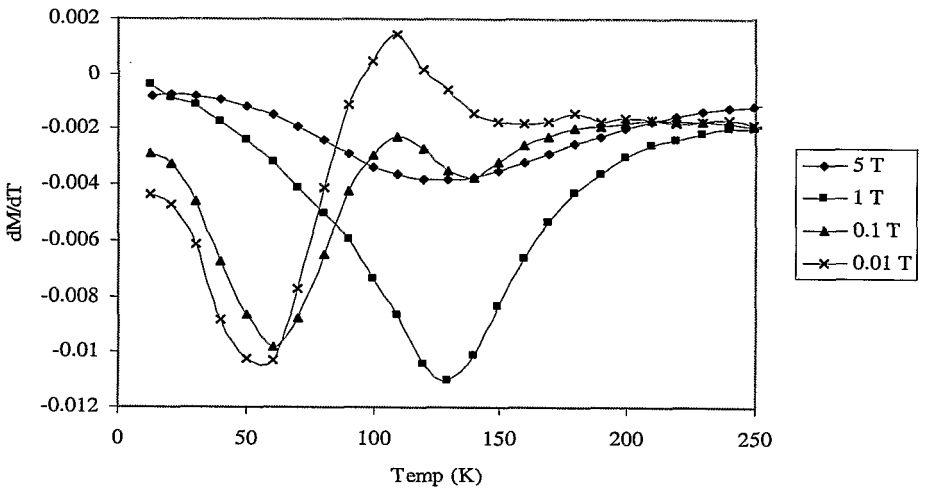

Figure 2: Derivative of the magnetisation curves for hot pressed NdFeB sample with various applied fields. The minimum in dM/dT signals the spin reorientation.

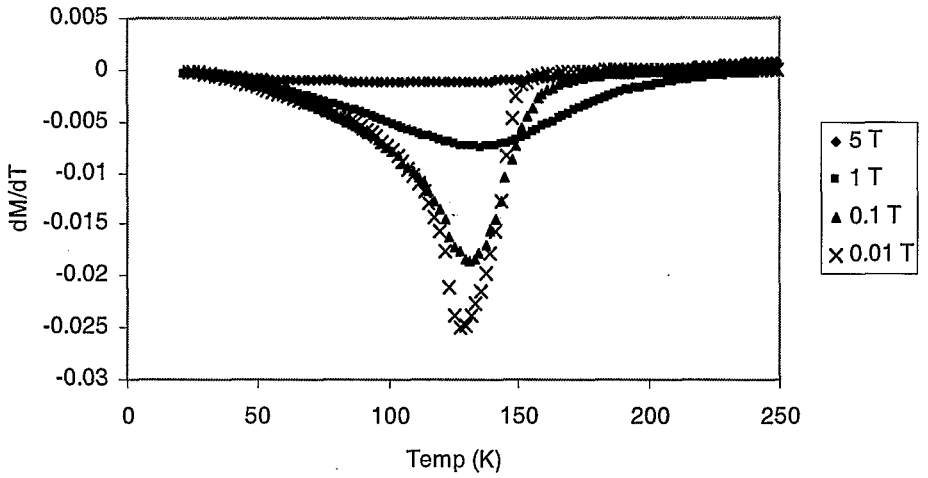

Figure 3: Derivative of the magnetisation curves for a NdFeB single crystal with various applied fields. The minimum in dM/dT signals the spin reorientation.

It can be seen from Fig. 2 and Table 1 that the determined spin reorientation temperature depends on the applied magnetic field in the nanoscaled samples. However, the results from the large-grained samples (single crystal and sintered) indicate that T_s does not change with changing applied field during measurement. An insight into these results can be obtained by an examination of the effect of applied field on the energetics of the system.

3.1 A Model of the Spin Reorientation

In order to gain insight into the underlying reason for the discrepancy in the spin reorientation temperatures measured under the influence of varying applied magnetic fields, it was desired to model the behaviour of the system within the constraints of the measurement geometry of the system. The following model is based on that of Christodoulou *et al.* [9] and is applied an ideally-aligned uniaxial ferromagnetic system.

The total energy of the ferromagnetic system under the influence of an applied magnetic field may be written as:

$$E_{tot} = E_0 + k_1 \cdot \sin^2 \varphi + \left(k_2 + k_3 \cdot \cos(4\theta)\right) \cdot \sin^4 \varphi - \vec{H}_{appl} \bullet \vec{M}_S \qquad (1)$$

where E_0 is the ground-state energy of the system, k_i (i = 1,2,3) are the i^{th}-order anisotropy constants for the $Nd_2Fe_{14}B$ compound, φ and θ describe the angles between the total moment $\vec{M}_S$ and the alignment direction, and $\vec{H}_{appl}$ is the applied field. The inter- and intra-atomic energies, such as the exchange and the crystalline electric field energies, are included in the terms that describe the anisotropy. The equilibrium angle between the total moment $\vec{M}_S$ and the alignment direction at a given temperature, $\varphi(T)$, is determined by a minimization of the total energy $E_{tot}(T)$.

The spin reorientation occurs at that temperature for which the equilibrium angle φ changes discontinuously.

The most general and explicit expression that describes the energy of the system may now be represented as:

$$E_{tot} = E_0 + k_1 \sin^2\varphi + (k_2 + k_3\cos(4\theta))\sin^4\varphi - \left|\vec{H}_{appl}\right| \cdot \left|\vec{M}_S\right| \cdot (\sin\varphi \sin z \cos(\theta - \gamma) + \cos\varphi \cos z) \quad (2)$$

where z describes the angle between the alignment direction and the applied field $\vec{H}_{appl}$, γ describes the angle between the alignment direction and the magnetization direction. The angle between the applied field $\vec{H}_{appl}$ and the magnetization $\vec{M}_S$ is equal to ω. To mimic the geometry of the system studied, z=90° and k_3 is assumed to be equal to zero. Eq. (2) is then reduced to

$$E_{tot} = E_0 + k_1 \cdot \sin^2\varphi + k_2 \cdot \sin^4\varphi - \left|\vec{H}\right| \cdot \left|\vec{M}_s\right| \cdot (\sin\varphi \cdot \cos(\theta - \gamma)) \quad (3)$$

When Eq. (3) is minimized with respect to θ the only non-trivial result is that the energy E_{tot} is minimized when $\theta = 90°$. Thus the equation to be evaluated is that produced by the minimization of Eq. (2) with respect to φ. This operation yields Eq. (4a), below:

$$\left[\frac{\partial E_{tot}}{\partial \varphi}\right]_{\theta=90°} = 2k_1 \sin\varphi\cos\varphi + 4k_2 \sin^3\varphi\cos\varphi - \left|\vec{H}_{appl}\right| \cdot \left|\vec{M}_S\right| \cos\varphi = 0 \quad 4(a)$$

which may be rewritten as:

$$2k_1 \sin\varphi + 4k_2 \sin^3\varphi - \left|\vec{H}\right| \cdot \left|\vec{M}_s\right| = 0 \quad 4(b)$$

Equation 4(b) was evaluated numerically to solve for the equilibrium angle φ as a function of temperature T for the end-member (x=0) compound $Nd_2Fe_{14}B$. The values of the anisotropy constants k_1 and k_2 as a function of temperature obtained on sintered samples were taken from Reference 10 and the temperature-dependent saturation magnetization $\vec{M}_S$ measured from a single crystal was obtained from Reference 11. The results of the calculated equilibrium cone angle φ for the applied fields $\vec{H}_{appl}$ equals 5 T, 1 T and 0.01 at T ~ 0 K is near 25 degrees, in general agreement with that measured for single-crystal and large-grained samples [1,12]. The calculated spin reorientation temperatures are marked by the rapid increase in φ in the vicinity of 130 - 140 K and show very little dependence on applied field.

The observed insensitivity of T_s to applied field was also found to be the case in calculations of magnetic properties of $Nd_2Fe_{14}B$ by Yehia and Aly [13] who found that the spin reorientation temperature did not show any field dependence in simulated M versus T relations at 0.1 and 0.5 T.

The experimental results of this work demonstrate that when the grain size is reduced into the nanocrystalline regime (MQPA and hot pressed sample), T_s shows a strong field dependence. In both cases, the T_s measured at low fields is ~60 K, significantly reduced from the high field values. The T_s of MQPA for H_{app} = 5 T is the same as that measured by Kou *et al.* for nanocrystalline melt-spun $Nd_2Fe_{14}B$ [4]. In nanocrystalline NdFeB samples the surface-to-volume ratio increases to create significant inter-grain magnetic exchange coupling. Zhang *et al.* [14] calculated that the effective anisotropy constant K_1^{eff} decreased when inter-grain exchange

coupling was present. Thus it is possible for intrinsic properties to vary between nanocrystalline and microcrystalline materials of the same composition. In $Nd_2Fe_{14}B$ spin reorientation occurs when $K_1^{eff} = 0$; this point is shifted to lower temperatures in nanocrystalline NdFeB due to strong exchange coupling [14]. The hot-pressed sample with a larger average nanograin size is expected to possess a smaller degree of exchange coupling and the effect of exchange coupling in this sample on T_s will not be as strong. This supposition is supported by the experimental results that T_s for the hot-pressed sample is lower than that of the large grained samples but is higher than that of the nanocrystalline MQPA sample.

A field-dependent T_s is only found in the nanoscale samples, which would lead to the conclusion that inter-grain exchange coupling underlies this effect. As the applied field is reduced T_s shifts to lower temperatures. A possible explanation for the observed behavior of the nanoscale $Nd_2Fe_{14}B$ system in this study may be found in the work of Herzer [15 - 17] on the magnetic properties of nanocrystalline soft ferromagnets devitrified from transition-metal-rich metallic glasses. In these systems the grain size of the samples, on the order of 10 nm, is approximately three times smaller than the ferromagnetic exchange length $L_{ex}^0 \approx (A/K_1)^{1/2}$, where A is the exchange stiffness of the matrix compound and K_1 is the first-order anisotropy constant. The ferromagnetic exchange length is equivalent to the Bloch wall thickness. The consequence of this discrepancy in length scale is that the magnetization vector cannot follow the randomly-oriented easy axis of each individual grain, and mesoscopic interaction domains are formed. This situation is much like that found in remanence-enhanced nanoscale permanent magnets [18]. The interaction domain experiences an effective overall anisotropy that is an average vectorial sum of the anisotropies of the constituent grains, and is thus greatly reduced in magnitude. The exchange length L_{ex}^0 of the system studied in this work is on the order of 10 nm [19], which is smaller than the average grain size (Table 1). However, this situation still allows a shell of material with a thickness on the order of the exchange length to be influenced by the local anisotropy of a given grain, resulting in a reduced anisotropy in the same manner as described by Herzer. The application of an external field to an assembly of nanoscale grains must upset the inter-grain exchange coupling and allow the system to experience largely undiluted anisotropy values. However, the reduced spin reorientation temperatures reported for nanoscale $Nd_2Fe_{14}B$ materials [4] attests to the fact that some exchange coupling across the grain boundaries must always be present. As the applied normal field is reduced in magnitude, interaction domains are formed with correspondingly smaller averaged anisotropy values and hence lower spin reorientation temperatures.

4 Conclusions

DC magnetisation measurements made at various applied fields on single crystal, sintered and nanocrystalline NdFeB samples indicate that T_s remains constant with applied field for single crystal and sintered samples but decreases with decreasing applied field strengths for nanocrystalline forms of the material. This effect can be attributed to the effect of strong inter-grain exchange coupling in the nanoscale materials which reduces the anisotropy constant and hence T_s is moved to lower temperatures.

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